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Basic and applied research have continued on the thermodynamic properties of currently used high density/high energy fuels and of pure chemical compounds that may be constituents of high energy fuels of the future. Enthalpy of combustion was measured for three compounds that are constituents of current ramjet fuels--hexacyclic exo,exo-dihydrodinorbornadiene, hexacyclic endo, endo-dihydrodinorbornadiene and exo-tetrahydrodicyclopentadience (JP-10). Heat capacities of exo-tetrahydrodicyclopendtadience (JP-10) and RJ-6, a blend of JP-10 and the hydrogeneted dimers of norbornadiene, were measured by differ ential scanning calorimetry. Enthalpy of combustion was measured for two pure hydrocardons, 1,7-dimethylindan and 1,4-dimethyl-2-isobutylbenzene, that are expected to have high steric interaction energies of alkyl substit-uents in the ring structure, and measurements are in progress on 1-ethyl-8-methylnaphtalene and 1,6-dimethylindan, Results of present and earlier research sponsored by AFOSR were reported both orally and in journal articles.

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FINAL TECHNICAL SUMMARY REPORT

for the period

1 October 1979 - 30 September 1980

THERMODYNAMICS OF ORGANIC COMPOUNDS

Bartlesville Energy Technology Center
Department of Energy
Bartlesville, Oklahoma

Research sponsored by:

Air Force Office of Scientific Research (NA)
Department of the Air Force

Contract No. AFOSR-ISSA-80-00004
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FINAL TECHNICAL SUMMARY REPORT

THERMODYNAMICS OF ORGANIC COMPOUNDS

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Bartlesville Energy Technology Center
Department of Energy
Bartlesville, Oklahoma

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* Synthesis and purification of research samples were provided by Professor E. J. Eisenbraun, Oklahoma State University. Samples were produced by purchase agreement for this project.

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FOREWORD

This research program consists of an integrated and interrelated effort of basic and applied research in chemical thermodynamics and thermcchemistry. Knowledge of variation of physical and thermodynamic properties with molecular structure is used to select compounds for study that because of high ring strain or unusual steric effects may have good energy characteristics per unit volume or per unit mass and thus be useful in the synthesis of high energy fuels. These materials are synthesized, and their thermodynamic properties are evaluated. In cooperation with researchers at Wright-Patterson Air Force Base, ramjet fuels currently in use are subjected to careful thermodynamic evaluation by measurements of heat capacity, enthalpy of combustion and vapor pressure.

Key words: ramjet fuels; ring compounds; combustion; enthalpy; hydrocarbons; high energy fuels; [illegible]

ABSTRACT

Basic and applied research have continued on the thermodynamic properties of currently used high density/high energy fuels and of pure chemical compounds that may be constituents of high energy fuels of the future.

Enthalpy of combustion was measured for three compounds that are constituents of current ramjet fuels--hexacyclic *exo,exo*-dihydrodinorbornadiene, hexacyclic *endo,endo*-dihydrodinorbornadiene and *exo*-tetrahydrodicyclopentadiene (JP-10).

Heat capacities of *exo*-tetrahydrodicyclopentadiene (JP-10) and RJ-6, a blend of JP-10 and the hydrogenated dimers of norbornadiene, were measured by differential scanning calorimetry.

Enthalpy of combustion was measured for two pure hydrocarbons, 1,7-dimethylindan and 1,4-dimethyl-2-isobutylbenzene, that are expected to have high steric interaction energies of alkyl substituents in the ring structure, and measurements are in progress on 1-ethyl-8-methylnaphthalene and 1,6-dimethylindan.

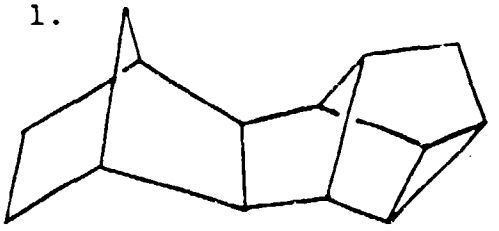
Results of present and earlier research sponsored by AFOSR were reported both orally and in journal articles.

1. NOMENCLATURE

This report describes research on the thermodynamic properties of several fuels and compounds of considerable molecular complexity. In an effort to facilitate understanding, the nomenclature and carbon skeletons of these materials follow in Table 1.

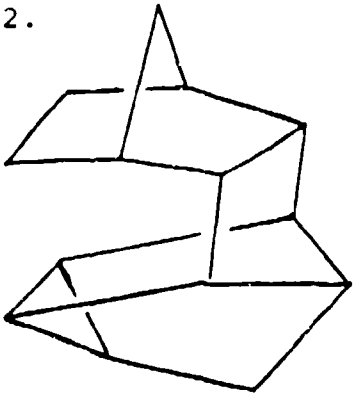
TABLE 1. Nomenclature of Materials

1.



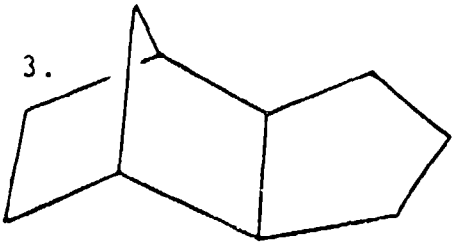
Hexacyclic
exo,exo-dihydro-
dinorbornadiene

2.



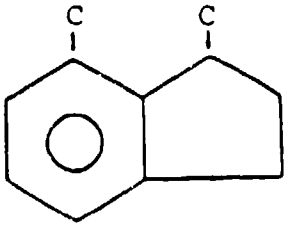
Hexacyclic
endo,endo-dihydro-
dinorbornadiene

3.



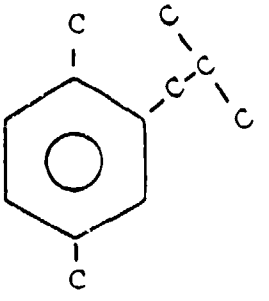
exo-Tetrahydro-
dicyclopentadiene

4.



1,7-Dimethyl-
indan

5.



1,4-Dimethyl-2-iso-
butylbenzene

2. ENTHALPY OF COMBUSTION

Material and Techniques

Two series of combustion experiments were performed. In the first series hexacyclic *exo,exo*-dihydrodinorbornadiene, hexacyclic *endo,endo*-dihydrodinorbornadiene, and *exo*-tetrahydrodicyclopentadiene were studied. These materials were supplied by Professor C. T. Moynihan of the Catholic University of America. They were prepared from concentrates obtained from Suntech, Incorporated, by triple recrystallization at -65° C from acetone and subsequent vacuum distillation. Gas chromatography of the two substances indicated the *exo,exo*- isomer to be 99.9 mole percent pure and the *endo,endo*- isomer to be 99.7 mole percent pure. Professor Moynihan also supplied a sample of *exo*-tetrahydrodicyclopentadiene, also obtained from Suntech, Incorporated, of 99.9 mole percent purity. These materials were used as received without further drying.

A second series of combustion calorimetric experiments involved 1,4-dimethyl-2-isobutylbenzene and 1,7-dimethylindan. The alkylbenzene was purified by the American Petroleum Institute Research Project 58 at Carnegie-Mellon University, A. J. Streiff, Director. The sample description given by API Project 58 lists the purity as 99.96 ± 0.01 mole percent. The alkylindan was prepared in the laboratories of Professor E. J. Eisenbraun at Oklahoma State University.

Carbon dioxide was recovered from the combustion products of most combustion experiments. Quantitative carbon dioxide recovery is an excellent indication that the materials are dry and free of all but isomeric impurity. Carbon dioxide recoveries for the two series of experiments and their companion benzoic acid calibration experiments are given in Table 2.

Fragile flexible ampoules[1,2] of borosilicate glass confined the liquid samples for combustion calorimetry; auxiliary oil (laboratory designation TKL 66) was used to initiate the combustion. Rotating-bomb calorimeter BMR II[3] and platinum-lined bomb PT-3b[4] were used without bomb rotation. For each experiment, 1 cm^3 of water was added to the bomb, and the

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1 W. D. Good and N. K. Smith, *J. Chem. Eng. Data*, 14, 102 (1969).

2 G. B. Guthrie, D. W. Scott, W. N. Hubbard, C. Katz, J. P. McCullough, M. E. Gross, K. D. Williamson and G. Waddington, *J. Am. Chem. Soc.*, 74, 4662 (1952).

3 W. D. Good, D. W. Scott and G. Waddington, *J. Phys. Chem.*, 60, 1080 (1956).

4 W. D. Good, D. R. Douslin, D. W. Scott, A. George, J. L. Lacina, J. P. Dawson and G. Waddington, *J. Phys. Chem.*, 63, 1133 (1959).

TABLE 2. Carbon Dioxide Recovery

Compound	Percent Recovery[a]
Hexacyclic *exo,exo*-dihydrodinorbornadiene (6)[b]	99.96 ± 0.01
Hexacyclic *endo,endo*-dihydrodinorbornadiene (7)	99.95 ± 0.01
exo-Tetrahydrodicyclopentadiene (4)	99.98 ± 0.03
Benzoic acid (8)	99.96 ± 0.02
1,7-Dimethylindan (8)	99.99 ± 0.01
1,4-Dimethyl-2-isobutylbenzene (6)	99.98 ± 0.02
Benzoic acid (8)	99.99 ± 0.00

[a] Mean and standard deviation of the mean.

[b] Number of experiments.

bomb was flushed and charged to 30 atm with oxygen. Each experiment was started at 296.15 K, and because the masses of combustibles were properly chosen, the final temperatures were very nearly 298.15 K. Temperatures were measured by quartz crystal thermometry; the quartz thermometer was calibrated with a platinum resistance thermometer. A programmable desktop calculator was used to control the combustion experiments and record the results. Readings were taken at 100-second intervals throughout the experiment; integration of the time-temperature curve is inherent in the quartz thermometer reading.

The experimental results are based on 1961 atomic weights.[5] For reducing weights in air to masses, converting the energy of the actual bomb process to that of the isothermal bomb process, and reducing to standard states,[6] the values of physical properties listed in Table 3 were used. The values of the densities of the hydrogenated dinorbornadienes and hydrogenated dicyclopentadiene are those of Moynihan.[7] The densities of 1,7-dimethylindan and 1,4-dimethyl-2-isobutylbenzene were derived from the masses of sample contained by ampoules of known volume. All values in parentheses are estimates.

National Bureau of Standards sample 39i benzoic acid was used for the two calibration series. The result of eight calibration experiments interspersed with the hydrogenated dibornadiene and dicyclopentadiene experiments was ε(calor) = 4007.28 ± 0.08 cal deg^{-1} (mean and standard deviation of the mean). The result of nine calibration experiments interspersed with the experiments with 1,7-dimethylindan and 1,4-dimethyl-2-isobutylbenzene was ε(calor) = 4007.40 ± 0.07 cal deg^{-1} (mean and standard deviation of the mean).

---

[5] A. E. Cameron and E. Wichers, *J. Am. Chem. Soc.*, 84, 4175 (1962).

[6] W. N. Hubbard, D. W. Scott and G. Waddington. In *Experimental Thermochemistry*, Chap. 5. F. D. Rossini, editor. Interscience: New York. 1956. pp. 75-128.

[7] C. T. Moynihan, H. Sasabe, D. S. Czaplak and U. E. Schnaus, *J. Chem. Eng. Data*, 23, 107 (1978).

TABLE 3. Physical Properties at 298.15 K

Compound	ρ	$(\partial E/\partial p)_T$	c_p
	g cm^{-3}	cal atm^{-1} g^{-1}	cal K^{-1} g^{-1}
Hexacyclic *exo,exo*-dihydro-dinorbornadiene	1.073	(-0.0029)	(0.3)
Hexacyclic *endo,endo*-dihydro-dinorbornadiene	1.085	(-0.0029)	(0.3)
exo-Tetrahydrodi-cyclopentadiene	0.931	(-0.0029)	(0.3)
1,7-Dimethylindan	0.93	(-0.0029)	(0.3)
1,4-Dimethyl-2-isobutylbenzene	0.836	(-0.0029)	(0.3)
Benzoic acid	1.32	-0.0028	0.289

Combustion Calorimetry Results

The following equations represent the combustion reaction for the compounds:

Hexacyclic *exo,exo*-dihydrodinorbornadiene and hexacyclic *endo,endo*-dihydrodinorbornadiene

$$C_{14}H_{18}(l) + 37/2\ O_2(g) = 14\ CO_2(g) + 9\ H_2O(l) \qquad (1)$$

exo-Tetrahydrodicyclopentadiene

$$C_{10}H_{16}(l) + 14\ O_2(g) = 10\ CO_2(g) + 8\ H_2O(l) \qquad (2)$$

1,7-Dimethylindan

$$C_{11}H_{14}(l) + 29/2\ O_2(g) = 11\ CO_2(g) + 7\ H_2O(l) \qquad (3)$$

1,4-Dimethyl-2-isobutylbenzene

$$C_{12}H_{18}(l) + 33/2\ O_2(g) = 12\ CO_2(g) + 9\ H_2O(l) \qquad (4)$$

Values of $\Delta E_c^\circ/m$ for all five compounds are given in Tables 4 through 8. All values of $\Delta E_c^\circ/m$ refer to the reaction of one gram of sample at 25° C. Derived molar values of the standard molar energy of the combustion reactions, ΔE_c°, and the standard molar enthalpy of combustion, ΔH_c°, are given in Table 9.

Uncertainty values are the "uncertainty interval" equal to twice the final overall standard deviation of the mean.

The formation reactions for the compounds from the elements follow.

Hexacyclic *exo,exo*-dihydrodinorbornadiene and hexacyclic *endo,endo*-dihydrodinorbornadiene

$$14\ C(c,\text{graphite}) + 9\ H_2(g) = C_{14}H_{18}(l \text{ or } g) \qquad (5)$$

exo-Tetrahydrodicyclopentadiene

$$10\ C(c,\text{graphite}) + 8\ H_2(g) = C_{10}H_{16}(l) \qquad (6)$$

TABLE 4. Summary of Calorimetric Experiments With Hexacyclic *exo,exo*-Dihydrodinorbornadiene[a]

(cal_{th} = 4.184 J)

	1	2	3	4	5	6
m'(compound)/g	0.692566	0.632900	0.680725	0.643644	0.663355	0.630626
m''(auxiliary oil)/g	0.076106	0.129905	0.084764	0.121109	0.100928	0.133413
m'''(fuse)/g	0.000937	0.001390	0.000946	0.001114	0.000906	0.000938
$n^i(H_2O)$/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c/K = (t_f - t_i + \Delta t_{corr})/K$	2.007103	2.000166	1.999089	2.003034	1.998326	2.002806
$\epsilon(calor)(-\Delta t_c)/cal_{th}$	-8043.02	-8015.22	-8010.91	-8026.72	-8007.85	-8025.80
$\epsilon(cont)(-\Delta t_c)/cal_{th}$[b]	-10.03	-10.07	-9.99	-9.95	-10.04	-10.14
$\Delta E_{ign}/cal_{th}$	0.18	0.18	0.18	0.18	0.18	0.18
$\Delta E_{dec}(HNO_3)/cal_{th}$	0.17	0.38	0.07	0.08	0.10	0.11
ΔE(corr to std states)/cal_{th}[c]	3.49	3.40	3.47	3.42	3.44	3.40
$\{-m''(\Delta E_c^\circ/m)$(auxiliary oil)$\}/cal_{th}$	837.50	1429.53	932.77	1332.73	1110.65	1468.13
$\{-m'''(\Delta E_c^\circ/m)$(fuse)$\}/cal_{th}$	3.79	5.63	3.83	4.51	3.67	3.80
$\{m'(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}$	-7207.92	-6586.17	-7080.58	-6695.75	-6899.85	-6560.32
$\{(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}\ g^{-1}$	-10407.56	-10406.34	-10401.53	-10402.88	-10401.44	-10402.87
$\{(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}\ g^{-1}$	-10403.77 ± 1.05 (mean and standard deviation of the mean)					

[a] The symbols and abbreviations of this table are those of W. N. Hubbard et al, *Experimental Thermochemistry*, Chap 5, pp. 75-128. F. D. Rossini, editor. Interscience: 1956.

[b] $\epsilon^i(cont)(t_i - 298.15\ K) + \epsilon^f(cont)(298.15\ K - t_f + \Delta t_{corr})$.

[c] Items 81 to 85, 87 to 90, 93 and 94 of the computation form of Hubbard et al (footnote a).

TABLE 5. Summary of Calorimetric Experiments With Hexacyclic *endo,endo*-Dihydrodinorbornadiene[a]

(cal_{th} = 4.184 J)

	1	2	3	4	5	6	7
m'(compound)/g	0.652947	0.661060	0.677778	0.685595	0.683514	0.682014	0.682267
m''(auxiliary oil)/g	0.109059	0.100517	0.085842	0.078907	0.080562	0.081030	0.081858
m'''(fuse)/g	0.001346	0.000984	0.001429	0.001104	0.000829	0.000883	0.000954
$n^i(H_2O)$/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c/K = (t_f - t_i + \Delta t_{corr})/K$	2.001078	1.997969	2.002148	2.002391	2.001245	1.999382	2.002284
ε(calor)$(-\Delta t_c)/cal_{th}$	-8018.88	-8006.42	-8023.16	-8024.14	-8019.55	-8012.08	-8023.71
ε(cont)$(-\Delta t_c)/cal_{th}$[b]	-10.08	-10.07	-9.93	-10.00	-10.00	-10.04	-9.99
$\Delta E_{ign}/cal_{th}$	0.18	0.18	0.18	0.18	0.18	0.18	0.18
$\Delta E_{dec}(HNO_3)/cal_{th}$	0.15	0.16	0.24	0.18	0.08	0.13	0.14
ΔE(corr to std states)$/cal_{th}$[c]	3.42	3.43	3.46	3.47	3.46	3.46	3.46
$[-m''(\Delta E_C^\circ/m)$(auxiliary oil)$]/cal_{th}$	1200.12	1106.13	944.64	868.32	886.53	891.69	900.80
$[-m'''(\Delta E_C^\circ/m)$(fuse)$]/cal_{th}$	5.45	3.98	5.79	4.47	3.36	3.57	3.86
$[m'(\Delta E_C^\circ/m)$(compound)$]/cal_{th}$	-6819.64	-6902.61	-7078.78	-7157.52	-7135.94	-7123.09	-7125.26
$[(\Delta E_C^\circ/m)$(compound)$]/cal_{th}\ g^{-1}$	-10444.40	-10441.73	-10444.10	-10439.87	-10440.08	-10444.20	-10443.51
$[(\Delta E_C^\circ/m)$(compound)$]/cal_{th}\ g^{-1}$	-10442.56 ± 0.75 (mean and standard deviation of the mean)						

[a] The symbols and abbreviations of this table are those of W. N. Hubbard et al, *Experimental Thermochemistry*, Chap. 5 pp. 75-128. F. D. Rossini, editor. Interscience: 1956.

[b] ε^i(cont)$(t_i - 298.15\ K) + \varepsilon^f$(cont)$(298.15\ K - t_f + \Delta t_{corr})$.

[c] Items 81 to 85, 87 to 90, 93 and 94 of the computation form of Hubbard et al (footnote a).

TABLE 6. Summary of Calorimetric Experiments With *exo*-Tetrahydrodicyclopentadiene[a]

(cal_{th} = 4.184 J)

	1	2	3	4	5	6
m'(compound)/g	0.709651	0.695413	0.683246	0.665336	0.660817	0.582034
m''(auxiliary oil)/g	0.040632	0.054945	0.065372	0.082981	0.086661	0.164243
m'''(fuse)/g	0.000998	0.001380	0.001224	0.001399	0.001474	0.001429
$n^i(H_2O)$/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c/K = (t_f - t_i + \Delta t_{corr})/K$	2.002666	2.004302	2.000068	2.001950	1.999687	2.002634
ϵ(calor)$(-\Delta t_c)/cal_{th}$	-8025.24	-8031.80	-8014.83	-8022.37	-8013.30	-8025.11
ϵ(cont)$(-\Delta t_c)/cal_{th}$[b]	-10.00	-10.02	-9.96	-8.63	-10.13	-8.76
$\Delta E_{ign}/cal_{th}$	0.18	0.18	0.18	0.18	0.18	0.18
$\Delta E_{dec}(HNO_3)/cal_{th}$	0.15	0.35	0.18	0.19	0.20	0.26
ΔE(corr to std states)$/cal_{th}$[c]	3.03	3.02	3.01	2.99	2.99	2.93
$\{-m''(\Delta E_c^\circ/m)$(auxiliary oil)$\}/cal_{th}$	447.13	604.64	719.38	913.16	953.65	1807.40
$\{-m'''(\Delta E_c^\circ/m)$(fuse)$\}/cal_{th}$	4.04	5.59	4.96	5.67	5.97	5.79
$\{m'(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}$	-7580.71	-7428.04	-7297.08	-7108.81	-7060.44	-6217.31
$\{(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}\ g^{-1}$	-10682.31	-10681.48	-10680.02	-10684.54	-10684.41	-10682.04
$\{(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}\ g^{-1}$	-10682.47 ± 0.71 (mean and standard deviation of the mean)					

[a] The symbols and abbreviations of this table are those of W. N. Hubbard et al, *Experimental Thermochemistry*, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: 1956.

[b] ϵ^i(cont)$(t_i - 298.15\ K) + \epsilon^f$(cont)$(298.15\ K - t_f + \Delta t_{corr})$.

[c] Items 81 to 85, 87 to 90, 93 and 94 of the computation form of Hubbard et al (footnote a).

TABLE 7. Summary of Calorimetric Experiments With 1,7-Dimethylindan[a]

(cal_{th} = 4.184 J)

	1	2	3	4	5	6	7	8
m'(compound)/g	0.693120	0.701879	0.702513	0.704488	0.705371	0.704564	0.707447	0.709814
m''(auxiliary oil)/g	0.083326	0.076565	0.075499	0.073255	0.073403	0.073324	0.071136	0.069150
m'''(fuse)/g	0.000867	0.001138	0.001563	0.001169	0.001129	0.001385	0.001514	0.001009
$n^1(H_2O)$/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c/K = (t_f - t_i + \Delta t_{corr})/K$	1.999569	2.003615	2.002673	2.001173	2.003886	2.002150	2.003541	2.003995
ϵ(calor)$(-\Delta t_c)/cal_{th}$	-8013.08	-8029.29	-8025.51	-8019.50	-8030.38	-8023.42	-8028.99	-8030.81
ϵ(cont)$(-\Delta t_c)/cal_{th}$[b]	-8.70	-8.76	-8.78	-8.71	-8.78	-8.70	-8.76	-8.78
$\Delta E_{ign}/cal_{th}$	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
$\Delta E_{dec}(HNO_3)/cal_{th}$	0.17	0.21	0.15	0.03	0.07	0.18	0.34	0.24
$\Delta E_{(corr\ to\ std\ states)}/cal_{th}$[c]	3.53	3.55	3.55	3.55	3.56	3.56	3.56	3.57
$\{-m''(\Delta E_c^\circ/m)$(auxiliary oil)$\}/cal_{th}$	916.95	842.56	830.83	806.13	807.76	806.89	782.81	760.95
$\{-m'''(\Delta E_c^\circ/m)$(fuse)$\}/cal_{th}$	3.51	4.61	6.33	4.73	4.57	5.61	6.13	4.09
$\{m'(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}$	-7097.44	-7186.94	-7193.25	-7213.59	-7223.02	-7215.70	-7244.73	-7270.56
$\{(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}\ g^{-1}$	-10239.84	-10239.57	-10239.31	-10239.48	-10240.03	-10241.37	-10240.67	-10242.91
$\{(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}\ g^{-1}$	-10240.40 ± 0.43 (mean and standard deviation of the mean)							

[a] The symbols and abbreviations of this table are those of W. N. Hubbard et al, *Experimental Thermochemistry*, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: 1956.

[b] ϵ^1(cont)$(t_i - 298.15\ K) + \epsilon^f$(cont)$(298.15\ K - t_f + \Delta t_{corr})$.

[c] Items 81 to 85, 87 to 90, 93 and 94 of the computation form of Hubbard et al (footnote a).

TABLE 8. Summary of Calorimetric Experiments With 1,4-Dimethyl-2-isobutylbenzene[a]

(cal_{th} = 4.184 J)

	1	2	3	4	5	6
m'(compound)/g	0.683943	0.705659	0.700350	0.705518	0.705477	0.706340
m''(auxiliary oil)/g	0.074882	0.054872	0.059812	0.055607	0.073525	0.053966
m'''(fuse)/g	0.000984	0.001077	0.001552	0.001041	0.000992	0.001248
$n^i(H_2O)$/mol	0.05535	0.05535	0.05535	0.05535	0.05535	0.05535
$\Delta t_c/K = (t_f - t_i + \Delta t_{corr})/K$	1.999903	2.002601	2.002920	2.004169	2.053260	2.002558
ϵ(calor)$(-\Delta t_c)/cal_{th}$	-8014.41	-8025.23	-8026.50	-8031.51	-8228.24	-8025.05
ϵ(cont)$(-\Delta t_c)/cal_{th}$[b]	-9.98	-8.79	-8.72	-8.72	-9.03	-8.71
$\Delta E_{ign}/cal_{th}$	0.18	0.18	0.18	0.18	0.18	0.18
$\Delta E_{dec}(HNO_3)/cal_{th}$	0.29	0.15	0.16	0.09	0.13	1.94
ΔE(corr to std states)$/cal_{th}$[c]	3.16	3.19	3.18	3.19	3.27	3.18
$\{-m''(\Delta E_c^\circ/m)$(auxiliary oil)$\}/cal_{th}$	824.03	603.84	658.20	611.92	809.10	593.86
$\{-m'''(\Delta E_c^\circ/m)$(fuse)$\}/cal_{th}$	3.98	4.36	6.29	4.22	4.02	5.05
$\{m'(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}$	-7392.75	-7422.30	-7367.21	-7420.63	-7420.57	-7429.55
$\{(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}\ g^{-1}$	-10516.59	-10518.25	-10519.33	-10517.99	-10518.51	-10518.38
$\{(\Delta E_c^\circ/m)$(compound)$\}/cal_{th}\ g^{-1}$	-10518.18 ± 0.37 (mean and standard deviation of the mean)					

[a] The symbols and abbreviations of this table are those of W. N. Hubbard et al, *Experimental Thermochemistry*, Chap. 5, pp. 75-128. F. D. Rossini, editor. Interscience: 1956.

[b] ϵ^i(cont)$(t_i - 298.15\ K) + \epsilon^f$(cont)$(298.15\ K - t_f + \Delta t_{corr})$.

[c] Items 81 to 85, 87 to 90, 93 and 94 of the computation form of Hubbard et al (footnote a).

TABLE 9. Derived Molar Values at 298.15 K

Compound	ΔE_c°	ΔH_c°
	kcal mol^{-1}	kcal mol^{-1}
Hexacyclic *exo,exo*-dihydrodinorbornadiene	-1938.22 ± 0.46	-1940.88 ± 0.46
Hexacyclic *endo,endo*-dihydrodinorbornadiene	-1945.44 ± 0.36	-1948.11 ± 0.36
exo-Tetrahydrodicyclopentadiene	-1455.37 ± 0.26	-1457.74 ± 0.26
1,7-Dimethylindan	-1497.50 ± 0.22	-1499.57 ± 0.22
1,4-Dimethyl-2-isobutylbenzene	-1706.86 ± 0.24	-1709.53 ± 0.24

1,7-Dimethylindan

$$11\ C(c,graphite) + 7\ H_2(g) = C_{11}H_{14}(l) \qquad (7)$$

1,4-Dimethyl-2-isobutylbenzene

$$12\ C(c,graphite) + 9\ H_2(g) = C_{12}H_{18}(l) \qquad (8)$$

Derived values of the enthalpy of formation for the five compounds are given in Table 10. Values of the enthalpy of vaporization of the two hydrogenated dimers of norbornadiene and of *exo*-tetrahydrodicyclopentadiene were provided by Dr. Margret Månsson of the University of Lund, Lund, Sweden. These values permit derivation of enthalpies of formation in the gaseous state. The enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ were taken to be -94.051 and -68.315 kcal mol^{-1}, respectively.[8] Uncertainties assigned were 0.011 kcal mol^{-1} for $CO_2(g)$,[9] and 0.010 kcal mol^{-1} for $H_2O(l)$.[10]

The values of uncertainty expressed in Table 10 are also the "uncertainty interval" and reflect uncertainties in the enthalpies of formation of gaseous CO_2 and liquid water as well as the combustion calorimetry.

It is of interest to note that the greater value of the enthalpy of formation of the *endo,endo*- dimer of hydrogenated norbornadiene is at least qualitatively what would be expected from the close proximity of the hydrogen atoms and their repulsions.

The value of the enthalpy of combustion of *exo*-tetrahydrodicyclopentadiene is in excellent agreement with a value obtained earlier in this laboratory on a sample of less certain purity.[11]

Combustion calorimetry of 1-ethyl-8-methylnaphthalene and 1,6-dimethylindan is in progress. When this study is completed, it will be possible to make an assessment of the magnitude of the steric interaction energies in the 1,8-alkyl substituted naphthalenes and the 1,7-alkyl substituted indans.

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[8] D. D. Wagman, W. H. Evans, I. Halow, V. B. Parker, S. M. Bailey and R. H. Schumm, *Natl. Bur. Stand. (U.S.) Tech Note 270-3*, 1968.

[9] F. D. Rossini and R. S. Jessup, *J. Res. Natl. Bur. Stand.*, 21, 491 (1938).

[10] F. D. Rossini, *J. Res. Natl. Bur. Stand.*, 6, 1 (1931).

[11] N. K. Smith and W. D. Good, *American Institute of Aeronautics and Astronautics Journal*, 17, No. 8, 905-907 (1979).

TABLE 10. Enthalpies of Formation at 298.15 K

Compound	State	ΔH_f°
		kcal mol^{-1}
Hexacyclic *exo,exo*-dihydro-dinorbornadiene	(l)	9.34 ± 0.49
	(g)	24.97 ± 0.50
Hexacyclic *endo,endo*-dihydro-dinorbornadiene	(l)	16.56 ± 0.40
	(g)	32.18 ± 0.41
exo-Tetrahydrodi-cyclopentadiene	(l)	-29.29 ± 0.29
	(g)	-17.65 ± 0.29
1,7-Dimethylindan	(l)	-13.20 ± 0.26
1,4-Dimethyl-2-isobutylbenzene	(l)	-33.92 ± 0.28

3. HEAT CAPACITIES OF RJ-6 AND JP-10

The heat capacities of JP-10 (*exo*-tetrahydrodicyclopentadiene) and RJ-6 (a blend of JP-10 and three hydrogenated dimers of norbornadienes) were measured on a Perkin-Elmer DSC-2 differential scanning calorimeter. Measurements had been made previously on these substances; however the results were suspect because Perkin-Elmer volatile sample pans were used. With these pans it is difficult to seal an adequate amount of liquid sample for accurate measurements. Also, results have been obtained with these pans for other liquids that incorrectly show maxima in plots of liquid heat capacities versus temperature. For these reasons new measurements were made in high pressure cells that were designed in part to overcome these problems.

Results were obtained on 25-mg samples from 260 K up to 465 K where the vapor pressure reaches about 2 atmospheres. Two methods of measurement were used with the high pressure cells: (1) the ordinary "displacement" method and (2) a "differential" method suggested by Cassel.[12] The temperature range was covered in two stages, 260-373.3 K and 335-465 K, so that the methods could be compared before the samples were heated to the boiling region. After results were obtained at the highest temperature, repeat measurements by method 2 for the lower temperature range gave results that agreed to within 0.5 percent of those obtained initially. This is believed to be evidence of lack of significant change in the samples during the study. The results from the two methods agreed to within 1 percent. The values selected and given below are those obtained from the differential, or substitution, method because it is inherently more accurate.

The heat capacities of the two fuels are represented by the following equations:

JP-10

$$C_p(\text{cal/g K}) = (0.10423 + 0.76872 \times 10^{-3}\ T + 0.46992 \times 10^{-6}\ T^2) \pm 0.00081 \quad \text{for } T = 260 \text{ to } 465 \text{ K} \qquad (9)$$

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[12] B. Cassel, Perkin-Elmer Corp., 1976. Text of presentation, "New Techniques in DSC: Differential Heat Capacity Determinations for Maximum Accuracy," at the Pittsburgh Conference on Analytical Chemistry, Cleveland, Ohio, March 1974.

$$C_p(\text{cal/g K}) = (0.013913 + 0.10963 \times 10^{-2}\ T) \pm 0.00056 \quad \text{for } T = 260 \text{ to } 465 \text{ K} \qquad (10)$$

where uncertainties are standard deviations at either end of the measurement range.

The new results as well as those obtained previously, in this laboratory and at the Catholic University of America[7,13] by C. T. Moynihan, are shown in Figures 1 and 2. The new values of heat capacity are believed to be reliable. The results for JP-10 turn upward as they should with increasing temperature. Also, the values of RJ-6 are lower and essentially linear with temperature as would be expected by the modifications produced by introducing the higher molecular weight, hydrogenated dimers of norbornadienes into the JP-10.

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[13] C. T. Moynihan, private communication, March 14, 1978.

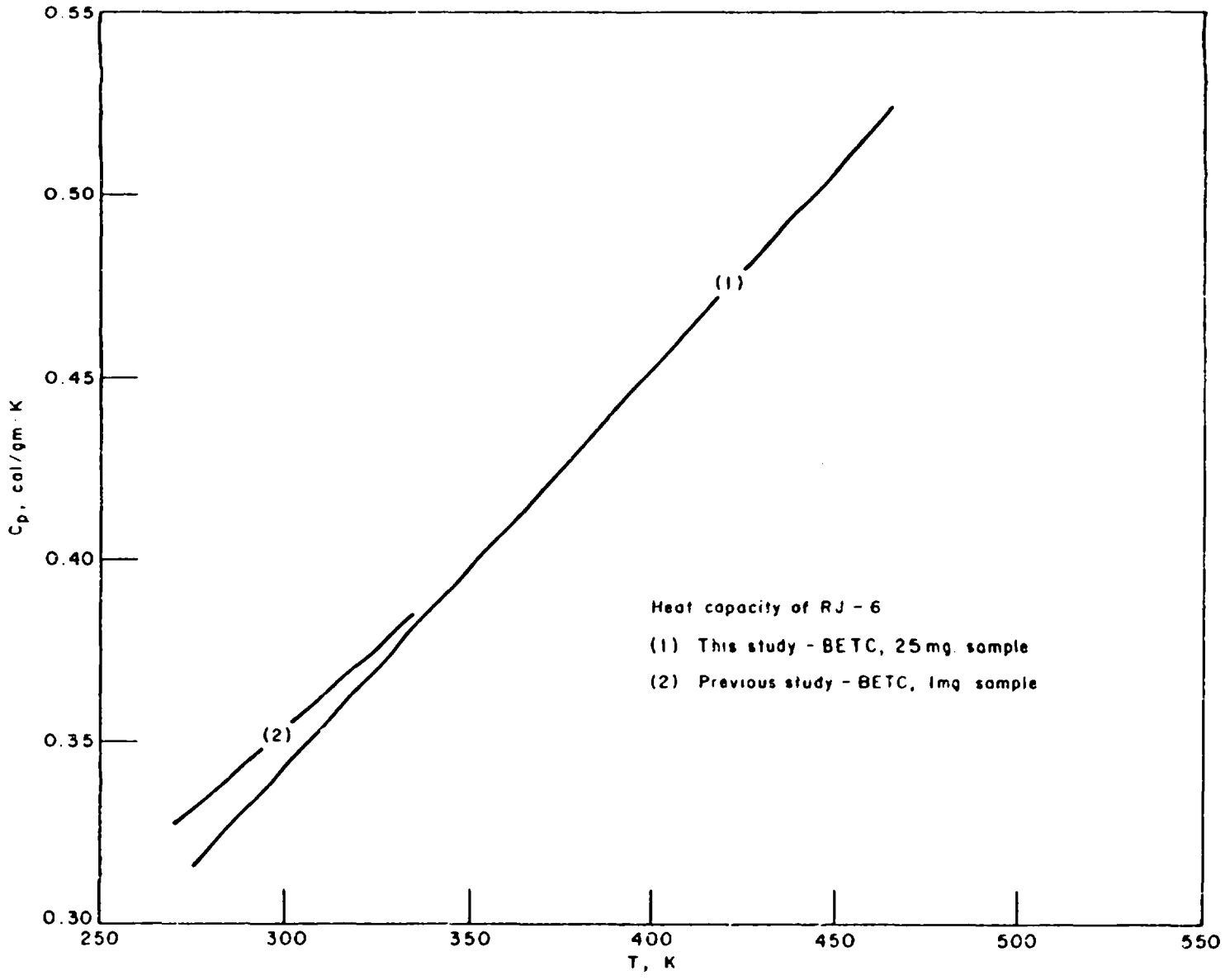

FIGURE 1. Comparison with other experimental heat capacities of RJ-6.

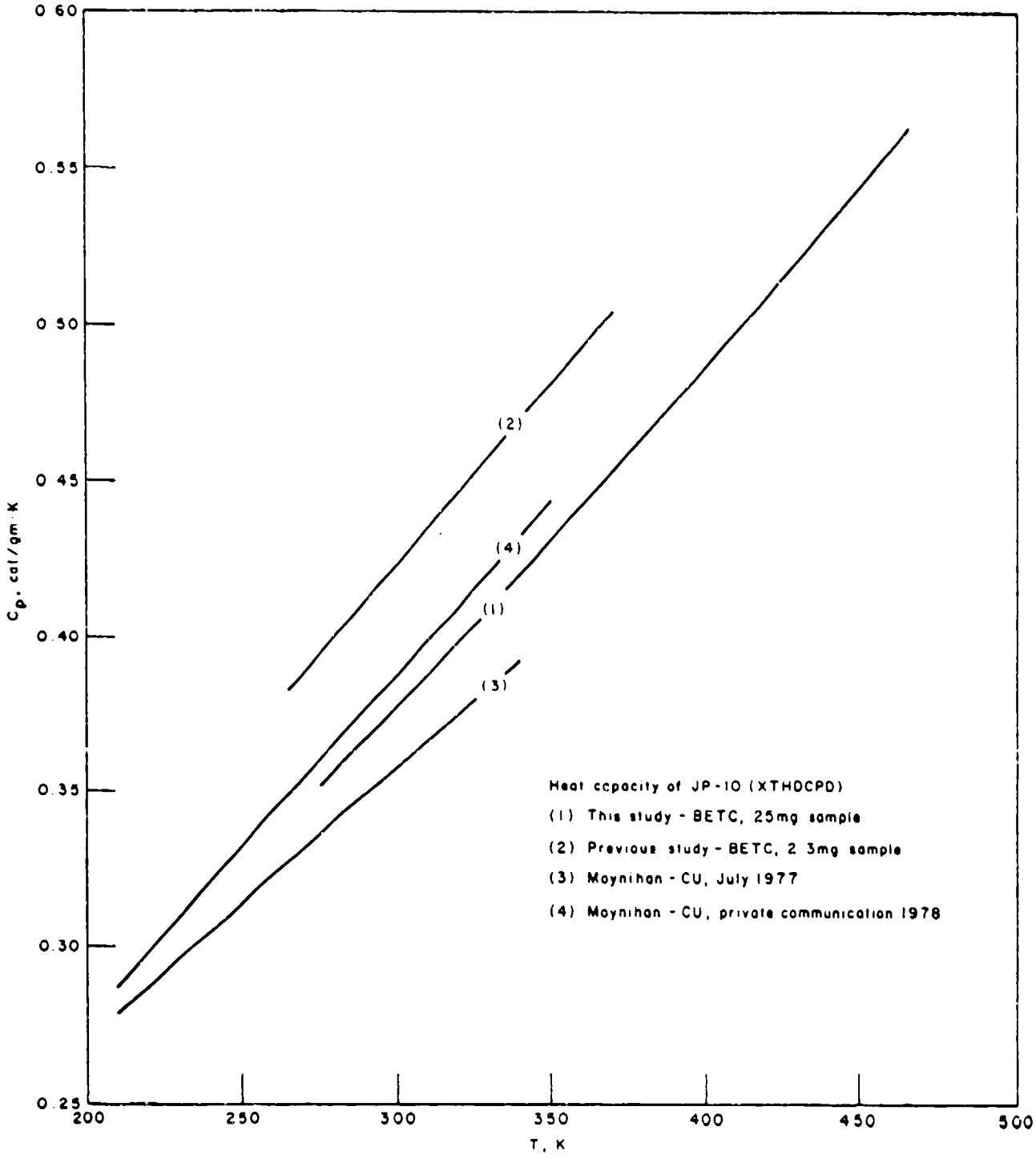

FIGURE 2. Comparison with other experimental heat capacities of JP-10.

4. PUBLICATIONS AND PRESENTATIONS

Thermodynamics of Organic Compounds presented by W. D. Good, AFOSR Contractors Meeting in Air-Breathing Combustion Dynamics, Alexandria, Va., Jan. 26-Feb. 1, 1980.

Vapor Pressure of 17 Miscellaneous Organic Compounds by A. G. Osborn and D. W. Scott. *Journal of Chemical Thermodynamics*, 12, No. 5, 429-438 (1980).

5. MANUSCRIPTS ACCEPTED FOR PUBLICATION

Thermodynamic Properties of Cyclopropylamine, Cyclopentylamine and Methylenecyclobutane by H. L. Finke, J. F. Messerly and S. H. Lee-Bechtold. Accepted by *Journal of Chemical Thermodynamics*.

Vapor Heat Capacities and Enthalpies of Vaporization of Six Miscellaneous Organic Compounds by I. A. Hossenlopp and D. W. Scott. Accepted by *Journal of Chemical Thermodynamics*.

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